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EMBRITTLEMENT OF NACL BY SURFACE
COMPOUND FORMATION

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**EMBRITTLEMENT OF NaCl BY SURFACE
COMPOUND FORMATION**

SECOND TECHNICAL REPORT

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by

W. H. Class

E. S. Machlin

G. T. Murray

**July 8, 1960
MRC NO. R168**

**Materials Research Corporation
47 Buena Vista Avenue
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ABSTRACT

The embrittling effects of oxygen, ozone, nitrogen, air, and surface residues, on NaCl has been investigated. The embrittlement by ozone and oxygen was found to be associated with the formation of a NaClO_3 surface compound. In these cases the initial crack that was responsible for fracture (in a bend test) always nucleated at the corners between the tension and side faces. The behavior of air was very erratic and on certain days did not produce embrittlement. During these periods, a short exposure to air of ozonated crystals would eliminate the previously induced embrittlement.

I. INTRODUCTION:

It was established many years ago¹ that considerable ductility could be obtained in NaCl single crystal specimens if the crystal surfaces were dissolved in water either during or immediately prior to the test. The original interpretation of this effect by Joffe attributed the enhanced ductility to the removal of surface microcracks by dissolution. Later investigations^{2, 3} have suggested that the exclusion of air from the specimen surface is the criterion for extensive plastic flow prior to fracture. The air embrittlement in this later work was associated with the diffusion of gaseous atoms into the surface layers of the crystal, thereby impeding the movement of dislocations. This model satisfactorily accounts for the re-embrittlement observed after further air exposure subsequent to the water dissolution treatment. However, the situation has recently become more complex by the observations in several laboratories^{4,5,6} that under certain conditions air exposure does not impair the ductility of NaCl. It has also been recognized⁵ that improper drying operations after water dissolution can leave surface precipitates that lead to embrittlement.

Cleavage defects on as-cleaved crystals can often be another source of embrittlement.

In the present work the effect of the gaseous atmospheres nitrogen, argon, air, oxygen, and ozone, on the ductility of rock salt was studied extensively. The embrittlement resulting from oxygen and ozone exposures was found to be associated with the formation of a NaClO_3 surface film. It is suggested that certain atmospheres, one of which often can be ambient air, which inhibit the formation or favor the decomposition of this compound, can promote ductility. Thus one aspect of the Joffe effect is certainly related to the removal of surface compounds or complexes by water dissolution. The effect of surface precipitates that remain after drying operations and of cleavage defects were also studied. In neither of the latter cases was the embrittlement as severe as that found with a NaClO_3 surface layer.

II. PROCEDURE AND SPECIMEN PREPARATION:

The nature of the embrittlement produced by the agents mentioned above was studied by means of microscopy, mechanical testing, and x-ray diffraction.

Specimens were cleaved from large crystals of optical quality sodium chloride obtained from the Harshaw Chemical Company, and, except for those tested in the as-cleaved condition, were given a 15-20 second immersion in distilled water followed by a rinse in absolute methyl alcohol. The specimens were then blotted on a soft, absorbent paper, and placed in a stream of warm, dry air. Such a procedure was found to give a control surface which was microscopically free of residues. (A few crystals were intentionally painted with a concentrated NaCl solution in order to investigate the effect of surface residues).

Crystals prepared in the above manner were placed in a gas train where they could be exposed to the desired gases for pre-selected periods of time. For the oxygen and nitrogen exposures, pure reagent grade gases were employed. The ozone was provided in the form of an ozone-oxygen mixture (approximately 10% ozone) prepared by passing commercial grade oxygen over a strong ultraviolet light source. All gases were dried prior to their introduction into the train. Since argon was found to be completely inert in its behavior, it was periodically utilized to check the control surfaces as well as the condition of the gas train used for aging the specimens.

A small jig was constructed for the application of three-point bending to the crystal while its tension surface was being viewed microscopically. In many instances, it was possible to detect the origin of a crack in the tensile surface and observe its growth under the influence of the applied stress. In addition, the device was so arranged that it was possible to compute the strain at fracture. In such a manner, crystals in the as-cleaved, distilled water polished, ozone embrittled, and surface painted conditions, were examined.

Other mechanical tests were performed in three point bending under a protective bath of oil. The apparatus was so adjusted that the load could be applied to the specimen at a constant, continuous rate. All specimens were shaped on silk wet with distilled water until they were of a 0.140 inch square cross section.

The Debye-Scherrer x-ray diffraction technique was employed for the investigation of surface compound formation. In order to obtain as much surface area as possible, specimens were prepared by crushing crystals of Harshaw material. The resulting powder was then annealed at 700°C for one hour in a dynamic vacuum of approximately 10^{-4} mm Hg and subsequently exposed to

ozone for 0.25, 1.5, and 8 hours. Following this treatment the specimens were sealed in Duco cement to prevent further exposure to air. The specimens were then placed in a Debye-Scherrer camera.

III. EXPERIMENTAL RESULTS:

A. Bend Tests

The effect of aging in ozone upon the ductility of sodium chloride in three point bending is shown in Figure 1. In this and subsequent figures, the strain reported is that on the outer fibre of the bend specimen. It can be seen that the ductility of the rock salt single crystals decreased markedly upon a short exposure to ozone. The short time required for embrittlement coupled with the fact that the embrittlement can be removed by re-dissolution in distilled water, suggests that the embrittling mechanism is some type of a surface reaction. It was also found that the stress to fracture (as measured by M_c/I) decreased in a one to one correspondence with the strain to fracture. This effect is depicted in Figure 2. Although the elasticity relationship used for calculation of the stress is not valid in the plastic region, it nevertheless serves as a useful means for comparison.

The embrittlement effects of the gases ozone, oxygen, nitrogen, and air are shown in Figure 3. It was observed that ozone embrittled rock salt the most rapidly followed by oxygen, nitrogen, and air in descending order. Whenever a specimen was embrittled by any of the above gases, its stress to fracture was correspondingly low. The effects of the gases oxygen, ozone, and nitrogen were fairly reproducible provided that air was excluded from the specimen surface and the rate of stress application was not varied. However, as can be seen in Figures 1 and 3, air embrittlement was very erratic. In fact, on many days no air embrittlement was observed even after 24 hours exposure. To further test this anomalous air behavior, a series of crystals was aged in ozone sufficient to achieve the embrittled condition. One group was then allowed to age in the atmosphere, a second specimen in a dessicator, and a third group was tested immediately. It was found that on days when air embrittlement was negligible, a considerable restoration of ductility was obtained in the embrittled crystals merely as a result of exposure to air. The results of these tests are shown in Table I.

TABLE I

OUTER FIBRE STRAIN TO FRACTURE RESULTING FROM THE
INDICATED AGING
TREATMENTS

0.5 hour age in ozone	0.5 hour age in ozone followed by a 0.5 hour age in atmospheric air.	0.5 hour age in ozone followed by a 0.5 hour age in dessicated air.
2.00%	4.71%	7.50%
1.09%	6.39%	
1.41%	6.25%	
1.70%		

Since dessicated air gave results similar to those of atmospheric air, it is not believed that the water vapor content of the air is responsible for these restoration effects. Neither could there be found any relationship between the relative humidity and air embrittlement.

The embrittlement reported above was also found to be sensitive to the rate of loading (Figure 4). An increase in the rate of stress application resulted in a decrease in ductility for a given time of age. In fact, a rather sharp transition between ductile and brittle behavior was observed as the rate of stress application was increased. This transition is

shown in Figure 5 as a function of the testing temperature. (The average outer fibre strain rate is the ratio of the outer fibre strain to fracture to the time in the plastic region required to fracture. This does not imply that the tests were conducted at constant strain rates). It is interesting to observe that there is a definite lower limit to the amount of strain required to fracture. This strain (approximately 1.5%) is observed to be independent of temperature and loading rates. This lower limit agrees with that obtained on the aging curves of Figures 3 and 4. In addition, preliminary data on water polished unaged rock salt crystals indicates a similar transition at higher loading rates but with the same lower limit of strain required to fracture.

B. Restoration of Ductility

It has been previously reported⁷ that an air embrittled crystal becomes quite ductile when tested in air at 150°C. It was also established that this higher temperature ductility was not related to the removal of a surface film, since specimens so heated were brittle when subsequently tested at room temperature while protected from the atmosphere (the specimens were placed in a

protective oil bath immediately upon removal from the heat source). In the present work, however, it was found that ductility could be restored if the anneal was carried out in a dynamic vacuum followed by a quench in vacuum. A set of six crystals was exposed to oxygen for one hour. Three of these crystals were subsequently annealed at 150°C for one hour and quenched in oil in a dynamic vacuum of 5×10^{-4} mm Hg. The results are listed in Table II.

TABLE II

OUTER FIBRE STRAIN AT FRACTURE

No Anneal	Annealed in vacuo
1.8%	4.0%
1.1%	5.7%
1.9%	7.5%

The increase in ductility is apparent.

C. X-ray Results

Microscopic evidence of crystallite formation on the surface of NaCl single crystals was found after long ozone exposures (Figure 6). However, these crystallites were not observed after the much shorter aging periods found sufficient for embrittlement.

Since the formation of a surface compound during the early gaseous exposure was suspect of being associated with the embrittlement phenomenon, it was decided to examine ozonated NaCl powder by x-ray diffraction techniques. Harshaw crystals which had been crushed and annealed in a dynamic vacuum were exposed to ozone for periods of 0.25, 1.5 and 8 hours. The powder patterns of the 1.5 and 8 hour specimens exhibited very prominent NaClO_3 diffraction lines. The specimen exposed to ozone for 0.25 hours exhibited a few weak NaClO_3 lines. It was also observed that the position of the NaClO_3 (210) reflection was shifted in a manner corresponding to a crystallographic plane spacing less than normal. In addition, the (210) reflection of the NaClO_3 line was somewhat broadened.

It is known that the cleavage planes of NaCl are $\{100\}$ type planes. One would therefore expect that the powder would consist predominantly of little cubes with $\{100\}$ surfaces. Such an orientation would also place $\{200\}$ planes perpendicular to the surface since NaCl has a cubic structure. Now since the plane spacing of the NaClO_3 $\{210\}$ planes is just slightly larger than that of the NaCl $\{200\}$ planes, it is conceivable

that the NaClO_3 forms on the surfaces of the powder such that the (210) planes of the NaClO_3 are parallel with the (200) planes of the NaCl . (See sketch in Figure 7). One would therefore have a coherent layer of NaClO_3 on a crystal of NaCl , the interface of the two being a NaCl (001) plane. Since the (210) NaClO_3 plane spacing is slightly larger than that of the (200) NaCl spacing, the layer would be placed in a state of compression, a result which was experimentally observed. In addition, the rock salt single crystal would be placed in a state of tension, a condition which is very helpful to the nucleation of cracks.

D. Observations of Crack Formation

Microscopic observations were made with the aid of a device which allowed for the viewing of the tension surface (a $\{100\}$ type cleavage plane) of the bend specimen. On such a surface, the slip traces would occur as either lines running perpendicular to the specimen axis or at an angle of 45° to this axis.

The fracture surface of a ductile (water polished) rock salt crystal is shown in Figure 8. In this case the tension surface is at the top of the photograph. It can be seen that the fracture nucleated at a point

below the tensile surface. This is very similar to the fracture surface of a polished MgO crystal reported by Stokes, Johnston, and Li⁵. Compared with the ductile crystals, fracture in as-cleaved rock salt apparently results from the nucleation of cracks at cleavage defects on the surface of the specimen. Figure 9 shows an example of a crack on the tension surface of a bend specimen which originated at a cleavage step on the surface of the crystal.

In ozone aged crystals on the other hand it was found that crack formation commenced on the corner of the intersection of the tension face and the surface perpendicular to the bend axis. Figures 10 and 11 show typical cracks just prior to fracture growing in from the corner edge of the tensile surface. All brittle ozone aged crystals fractured in this manner in comparison to the behavior of the water polished crystals where fracture originated in the body of the material near the tensile surface and to the behavior of the as-cleaved crystals where fracture originated at a cleavage defect. Typical fracture surfaces of ozonated crystals are shown in Figures 12 and 13. The river patterns on these surfaces clearly show that fracture originated at the corners

of the tensile surface and the face perpendicular to it. Figure 13 is the fracture surface of the crystal depicted in Figure 10. This crystal was fractured in a stepwise manner by intermittent application of the stress. The concentric markings indicate the positions where the crack stopped. The surfaces were examined for cracks after the ozonating treatment and prior to stress application, however, cracks were never observed until after a small amount (e.g. 1.0%) of strain had been produced. Lad, et. al.⁸ on the other hand, have observed microcrack formation in NaCl after long air aging periods at room temperature.

Several ductile (water polished) specimens were painted on their tension surfaces with concentrated sodium chloride solutions and allowed to dry in a stream of warm, dry air, to produce residues similar to those reported by Stokes, Johnston and Li⁵ to be responsible for embrittlement. After strains of approximately 2 to 4% cracks appeared in the crystal originating from the rim of the residue region. Figures 14 and 15 show two stages of such a fracture (arrows indicate the crack which led to the ultimate fracture of the material). It is observed that the crack originates

at a point on the rim of the residue which appears as a broad irregular vertical line on the tensile surface being viewed. This crack was observed to propagate and result in the ultimate fracture of the crystal. Figure 16 shows the fracture surface of this specimen. Note how the river patterns converge to the region of the residue which in this photograph appears as a slight mound on the edge of the tensile surface. The embrittlement of the rock salt by surface residues was most effective when the entire tensile surface was painted. However, even in this case it was found that the embrittlement induced was less severe than for the ozonating treatment.

IV. DISCUSSION OF RESULTS:

The fact that plastic flow always precedes fracture (1.5% strain at the outer fibre), even in the embrittled crystals, implies that the embrittling effect of the gaseous agents is primarily to enhance the probability of fracture subsequent to plastic flow. As Parker et.al⁹ have shown, some amount of plastic flow must occur in bending before subsurface sources can operate to supply

dislocations which move out towards the surface.

(All surface generated dislocations move into the crystal in bending). It is likely therefore that the primary embrittling effect of the gases is either to form a layer against which pile-ups develop or to enhance the stress to fracture at pile-ups in the vicinity of the surface. The need for plastic flow prior to fracture in embrittled crystals implies that even if cracks produced by the embrittling atmosphere exist in the surface layers, such cracks cannot be responsible for the enhancement of the brittle behavior.

The observation that the initial crack in ozonized specimens always occurred at the corners between the tension face and side faces implies that the tensile stress in the layer just beneath the chlorate layer may be important in nucleating cracks. That is, the cracks seem to nucleate in the region having the highest value of tensile stress (applied plus coherent layer developed stress). The dimension over which the coherency stress acts is probably small so that it is important to crack nucleation but not to microcrack growth. Thus, the likelihood is that the mechanism of embrittlement by ozone and oxygen in rock salt is similar to the mechanism of surface layer embrittlement by oxide layers on metals (the nucleation of cracks at dislocation pile-ups) with the additional factor that the coherency stress enhances

the probability of fracture.

With the mechanism just described it is possible to explain the results as follows. The effect of aging time is to increase both the effectiveness of the barrier (the number of dislocations that can be supported in the pile-up without leakage) and the magnitude of the coherency stress. Conversely, the effect of reversal of embrittlement is believed due to either the removal of the surface layer or removal of the coherency stresses or both.

The quantitative effect of strain rate on the transition temperature is about the same as that found in body-centered-cubic metals such as iron. For example, according to either Cottrell⁽¹⁰⁾ or Louat⁽¹¹⁾ the effect of strain rate on the transition temperature in iron should be given by the relationship

$$\ln \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

with $Q \approx 0.22$ ev. (Cottrell⁽¹⁰⁾)

or $Q \approx 0.5$ (Louat⁽¹¹⁾)

Using Cottrell's value of Q a 90° C change in transition temperature is obtained for a tenfold change in strain rate. This dependence is about the same as that observed in these experiments with rock salt. Use of Louats values

for Q would make the strain rate sensitivity of the transition temperature in iron somewhat larger than for rock salt. Thus, it is reasonable to expect that similar mechanisms governing the ductile-brittle transition may exist in these materials.

With the assumption that the true strain rates are proportional to the apparent outer fibre loading rates, then an activation energy can be computed from the data shown in Figure 5. This value is that required to make the curves superimpose. The value obtained is 0.26 e.v. This value may be interpreted in terms of current fracture theories. In Stroh's theory⁽¹²⁾ it corresponds to the activation energy to operate a secondary source nearest the head of a pile-up. If crack growth rather than nucleation is controlling then it is the activation energy to operate a secondary source near the spearhead of the crack.

The effect of the embrittling reaction on the strain rate-transition temperature relationship has not been quantitatively evaluated. However, in the absence of a chlorate layer the transition from ductile to brittle behavior is much more gradual. It is believed that the sharp transition in the presence of a surface barrier is due to the higher probability of nucleating a supercritical crack there as compared to the crack nucleation condition existent in a "ductile" crystal.

The effect of nitrogen is to embrittle rock salt, although this embrittlement is not as severe as that for

ozone and oxygen. To check whether the effect was due to nitrogen rather than oxygen as an impurity in the nitrogen, powdered rock salt was exposed to the nitrogen for 30 minutes and x-ray diffraction patterns were taken. There was no positive evidence for the existence of a chlorate layer. It appears likely therefore that nitrogen is present as a dissolved impurity rather than as a component of a compound layer. The cracks in most tests nucleated on the tension surfaces but not on the specimen corners as in ozonated crystals. However, no tests were conducted to determine whether nitrogen was present as a dissolved impurity. Further work to evaluate the effect of nitrogen is necessary.

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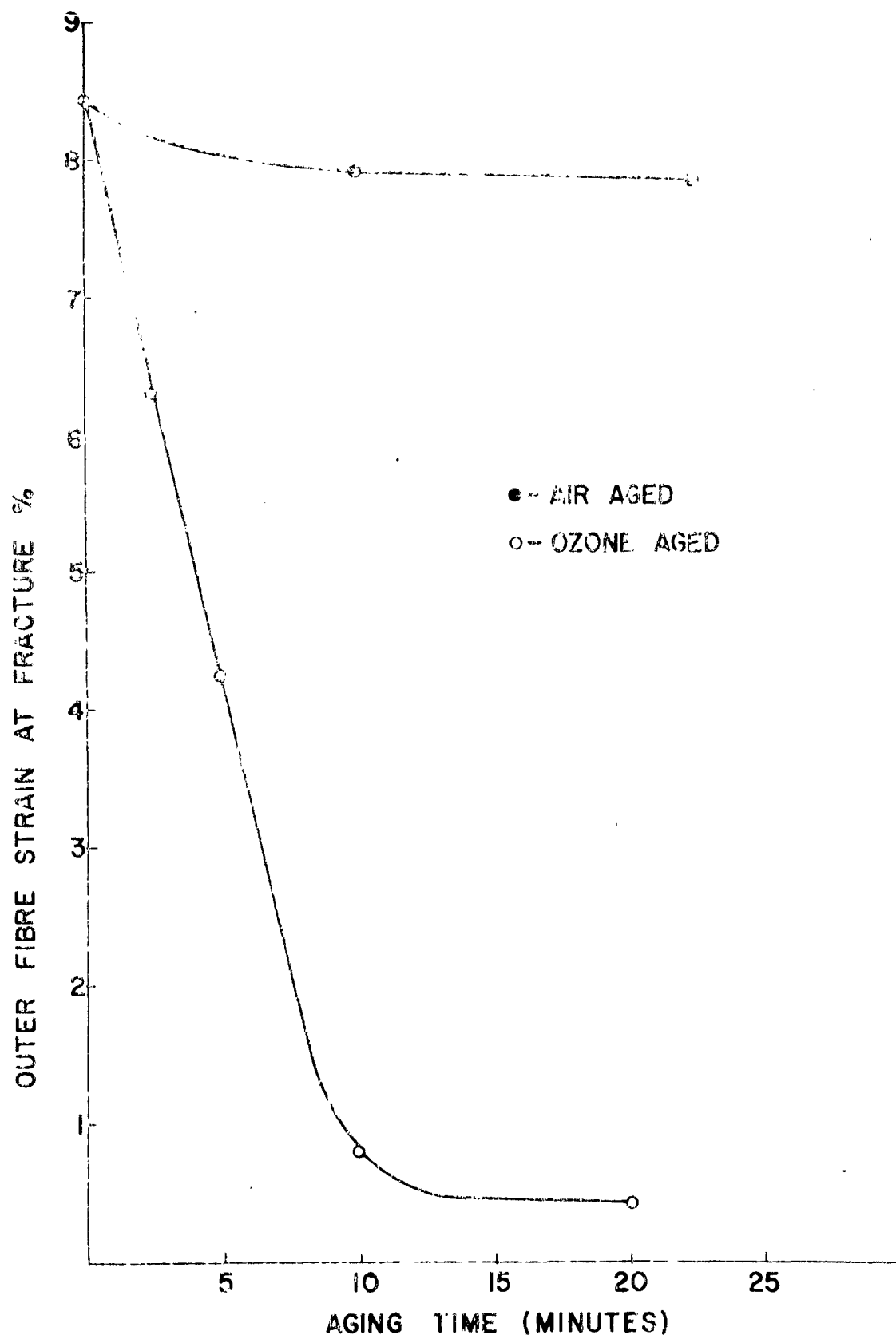
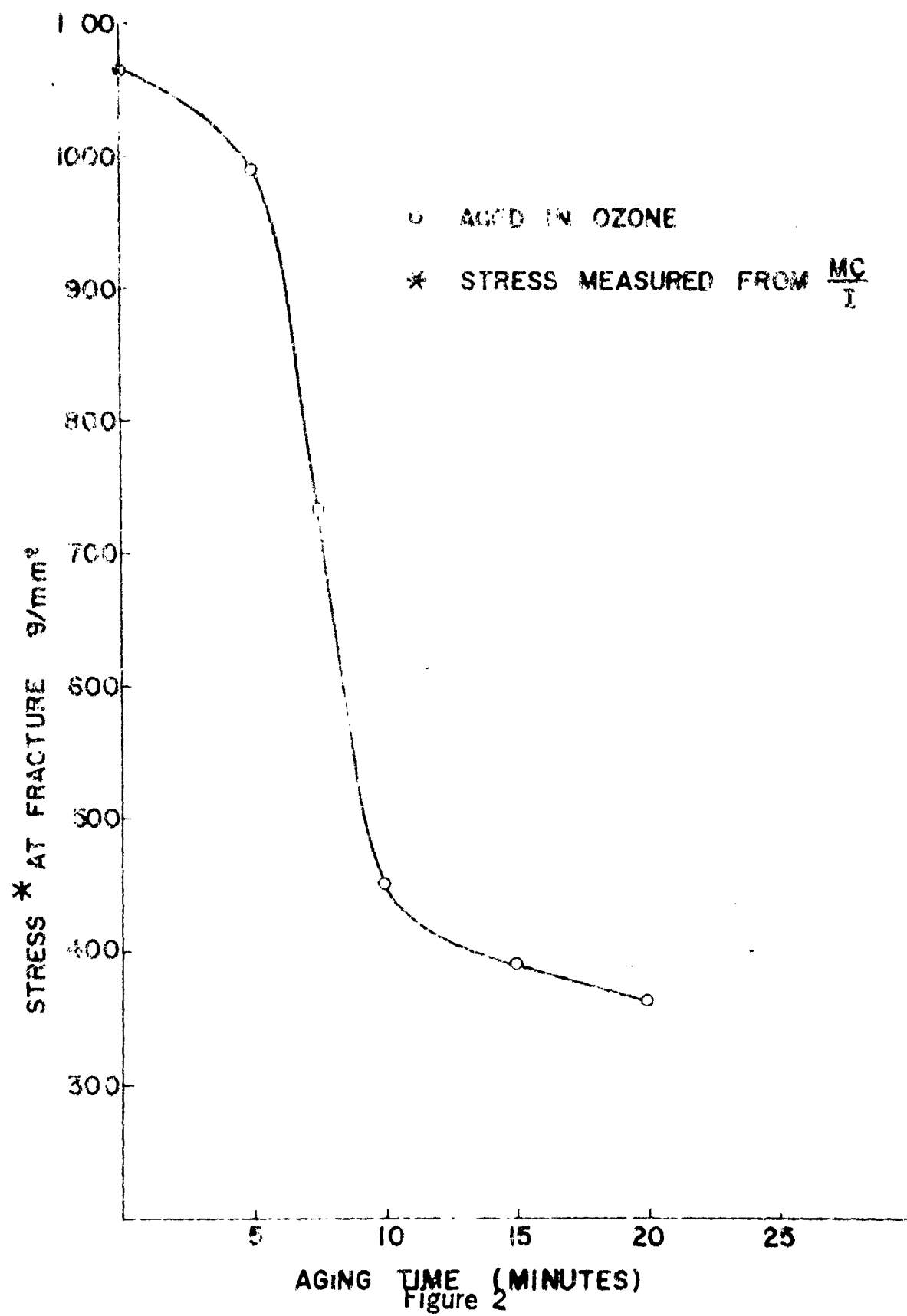


Figure 1



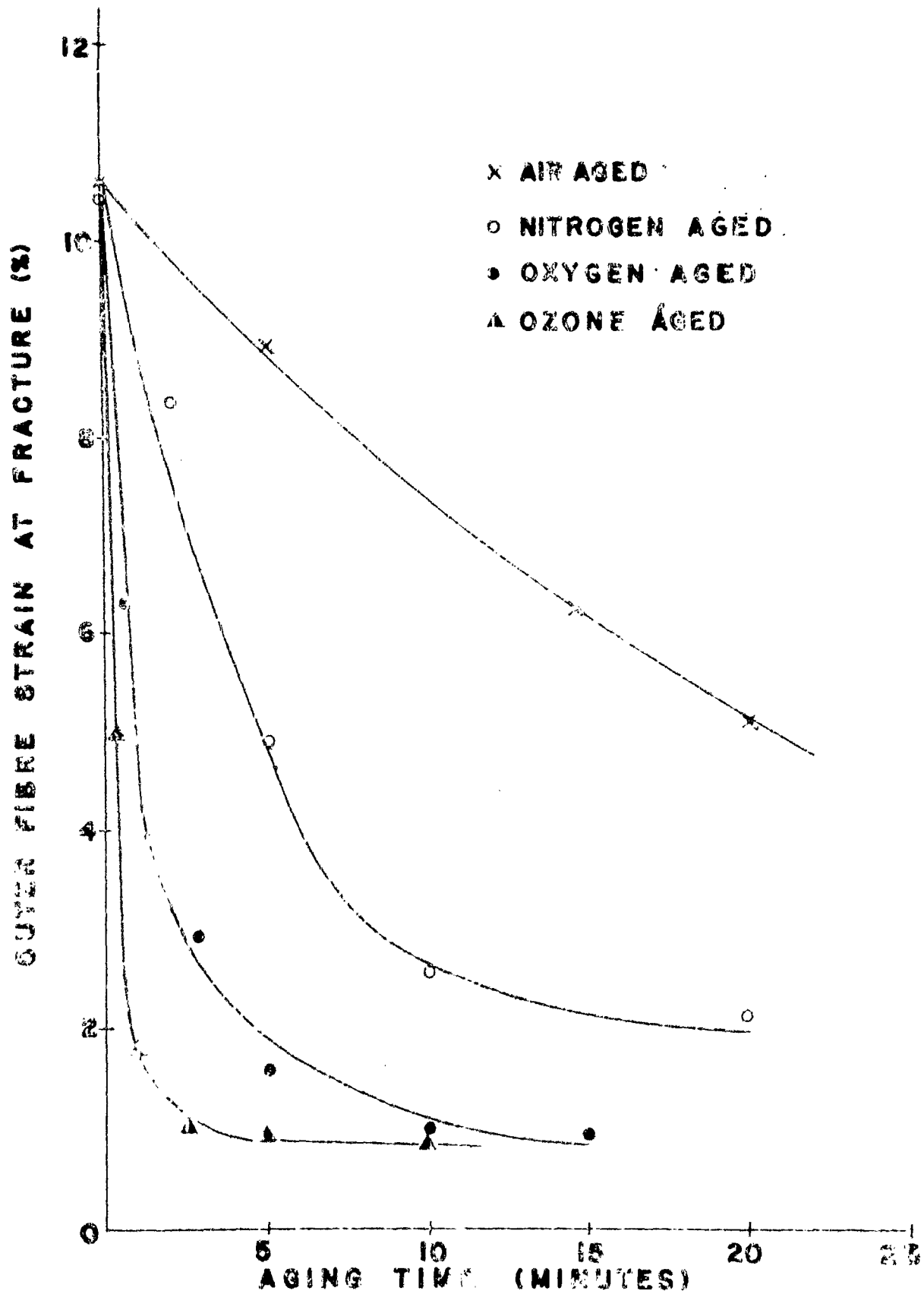


Figure 3

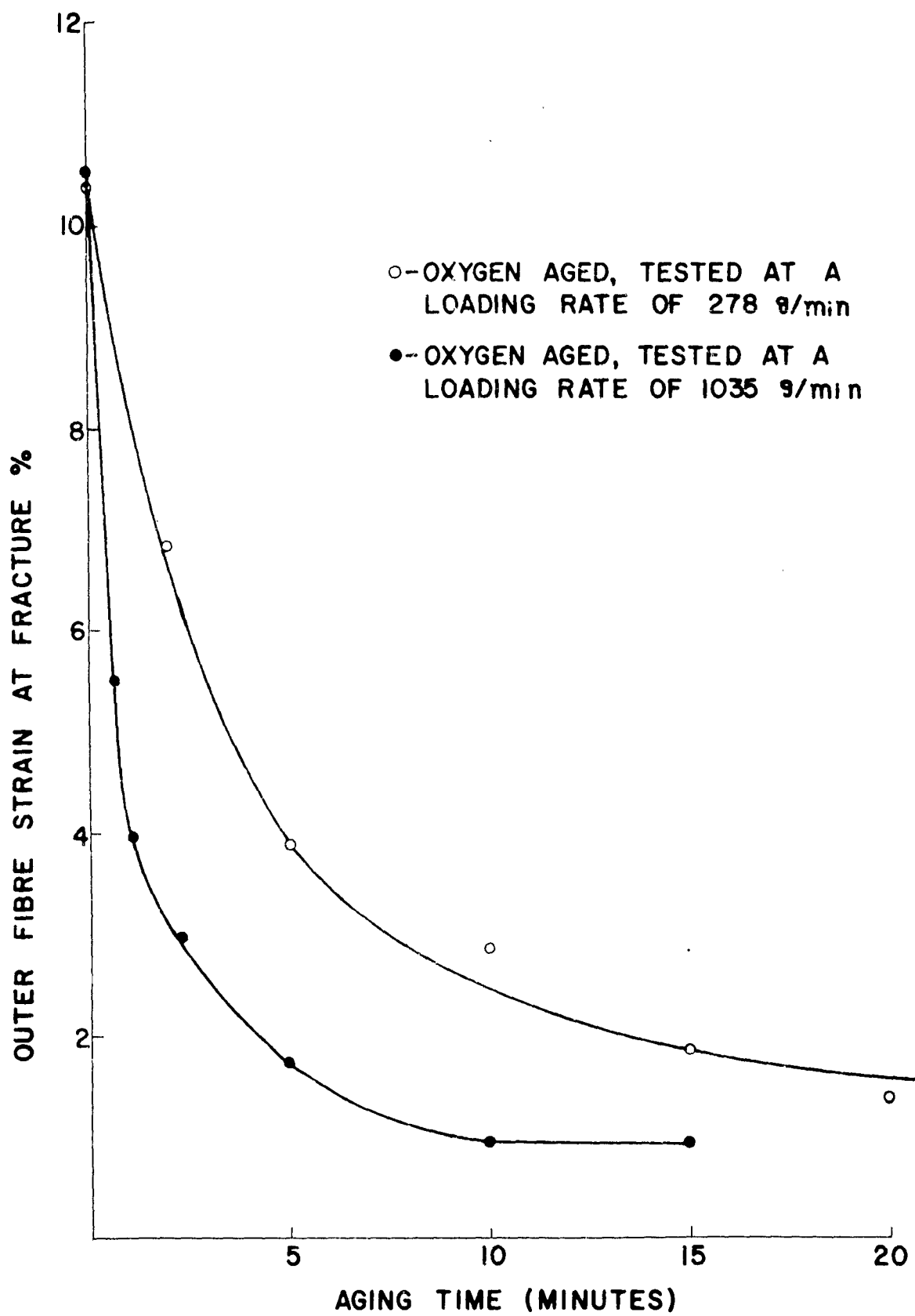


Figure 4

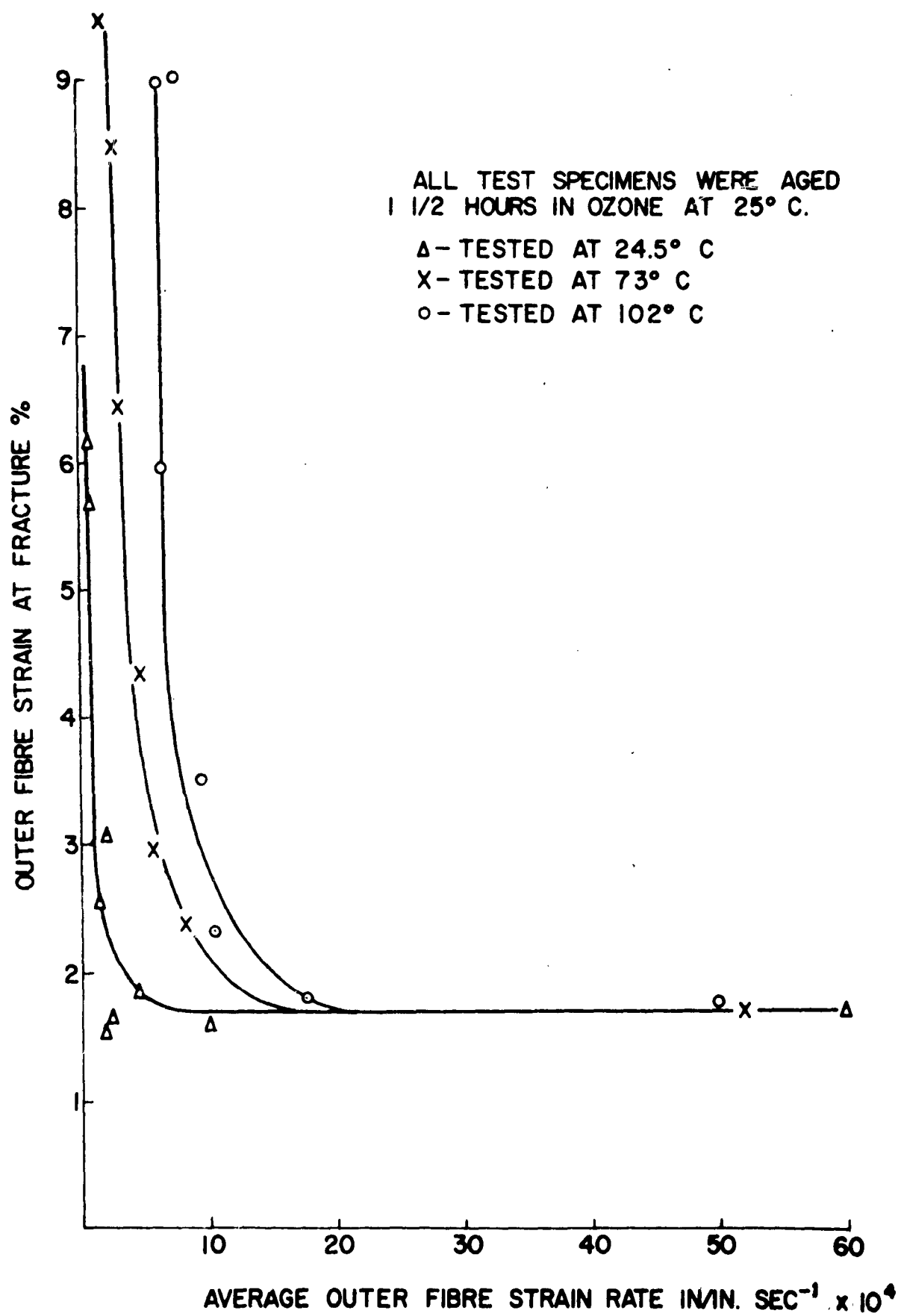


Figure 5

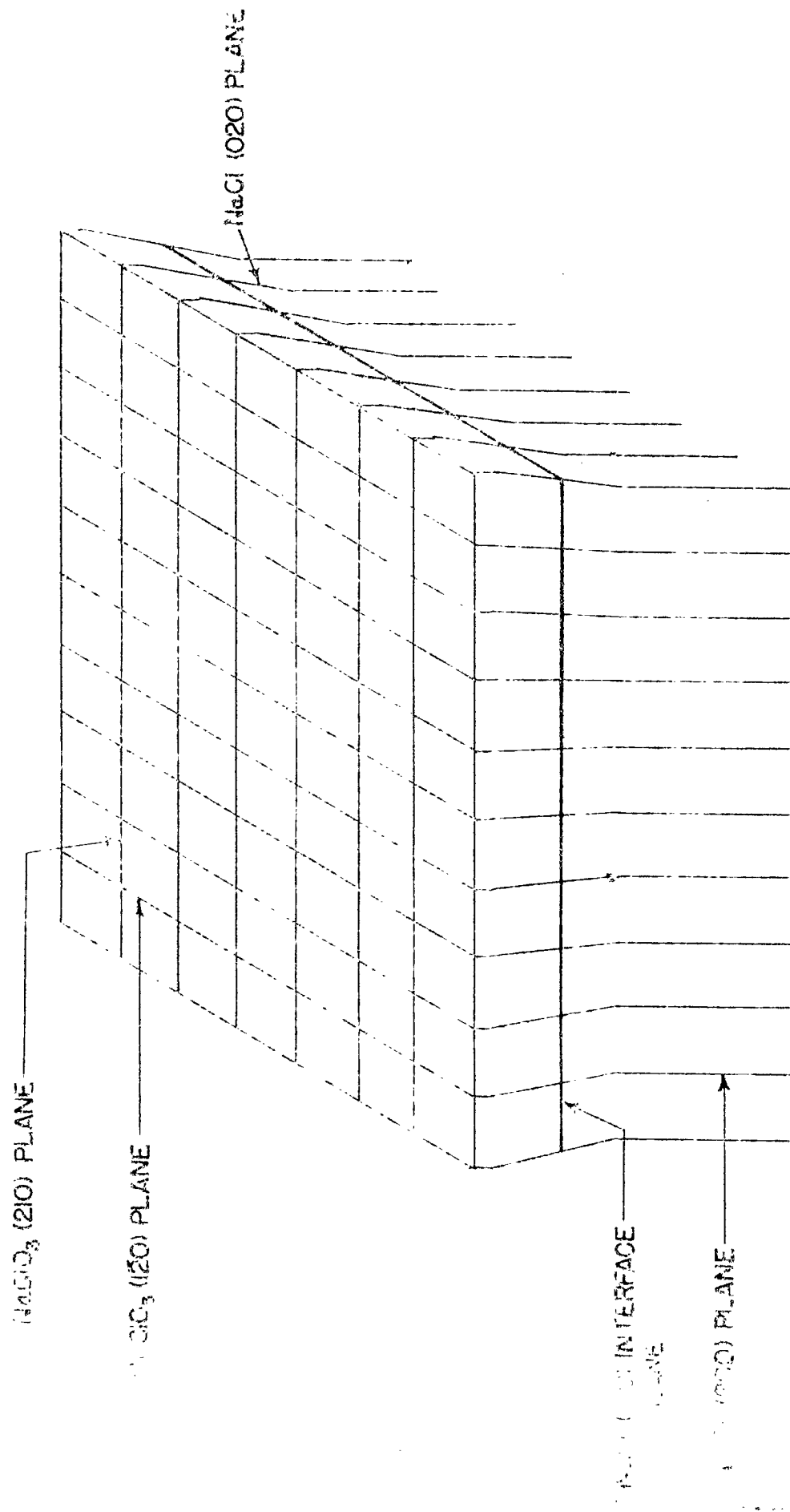


Figure 7

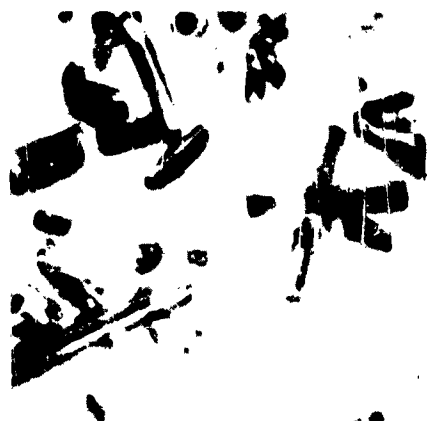


Figure 6. - Crystallites on
surface of ozonated crystal.
Mag. - 300X



Figure 8. Fracture surface,
Ductile crystal.
Mag. - 55X



Figure 9. - Crack formed at
Cleavage step.
Mag. - 50X



Figure 10. Crack Formed
at corner; ozonated crystal
Mag. - 100X



Figure 11. (Left)
Crack formed at
corner; ozonated crystal
Mag. - 55X



Figure 12. Fracture Surface
ozonated crystal
Mag. - 55X

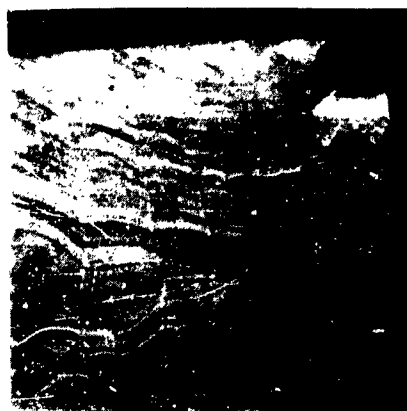


Figure 13. Fracture Surface
ozonated crystal
Mag. - 55X



Figure 14. Crack formed at
residue
Mag. - 90X

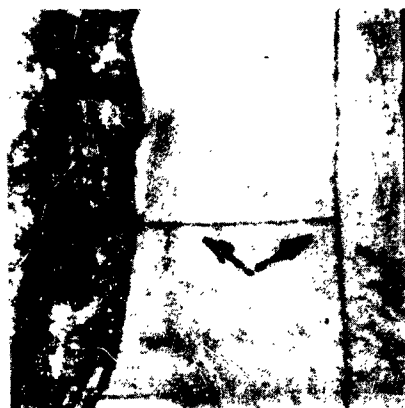


Figure 15. Growth of crack
in Figure 14
Mag. - 90X

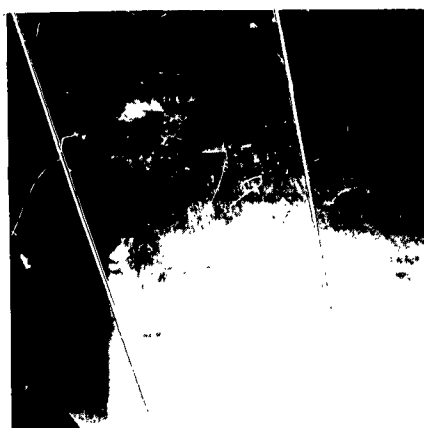


Figure 16. (Left) Fracture Surface
of crystal shown in
Figures 14 & 15
Mag. - 55X